

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 999 458 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
10.05.2000 Bulletin 2000/19(51) Int. Cl.⁷: G02B 1/10, G02B 1/11,
G02B 5/22

(21) Application number: 99119186.7

(22) Date of filing: 07.10.1999

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 07.10.1998 JP 28500198

(71) Applicants:
• Hitachi, Ltd.
Chiyoda-ku, Tokyo 101-8010 (JP)
• Hitachi Device Engineering Co., Ltd.
Mobara-shi, Chiba-ken 297-0037 (JP)(72) Inventors:
• Takao, Ishikawa
Hitachi-shi, Ibaraki 316-0025 (JP)
• Daigoro, Kamoto
Hitachi-shi, Ibaraki 316-0006 (JP)• Tomoji, Oishi
Hitachi-shi, Ibaraki 319-1417 (JP)• Ken, Tagahashi
Naka-gun, Ibaraki 319-1102 (JP)• Norikazu, Uchiyama
Awa-gun, Chiba 295-0004 (JP)• Kiyoshi, Miura
Mobara-shi, Chiba 297-0037 (JP)• Masahiro, Nishizawa
Mobara-shi, Chiba 297-0035 (JP)• Toshio, Tojo
Chosetsu-gun, Chiba 299-4315 (JP)

(74) Representative:

Beetz & Partner
Patentanwälte
Steinsdorfstrasse 10
80538 München (DE)

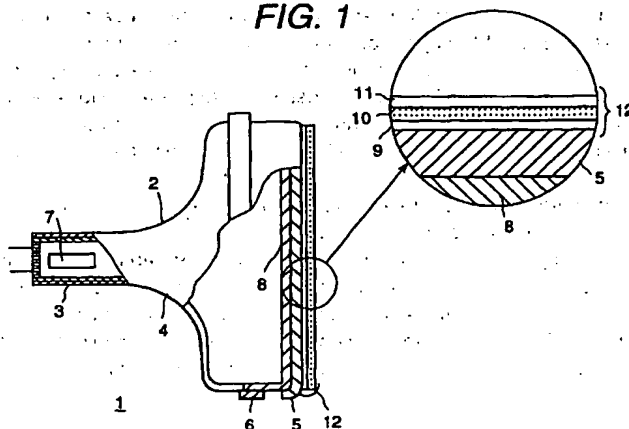
(54) Display apparatus with antistatic and antireflection laminated film

(57) A high definition display apparatus (1) having a wavelength selective absorption effect and an anti-static and anti-reflection effect is provided by thin films (9, 10, 11) having a low resistance and a high refractive index.

A high definition display apparatus (1) having an anti-static and anti-reflection film (10, 11) composed of laminating oxide or metallic thin films, wherein at least three layers of oxide or metallic films (9, 10, 11) having

different reflectance each other are laminated onto the front surface (5) of the display apparatus (1), the laminated films (9, 10, 11) are composed in a manner that an absorbing film (9) containing coloring material is arranged under a high reflectance film (10, 11), in view from the outer surface of the laminated films (9, 10, 11).

FIG. 1



EP 0 999 458 A2

Description

BACKGROUND OF THE INVENTION

[0001] In order to obtain the high definition display apparatus, various surface treatment films have been formed on surface of the display plane. For instance, an anti-static anti-reflection film was formed as disclosed in JP-A-4-334853 (1992). Furthermore, a wavelength selective absorption film, which absorbed side bands of emission spectrum selectively by adding coloring material for improving color purity of an emitter, was formed as disclosed in JP-A-4-144733 (1992), because the emission spectrum of RGB emission of the Braun tube was wide and bleeding of color was generated.

[0002] One of the anti-static anti-reflection films is formed by laminating oxide thin films having a different refractive index each other, in order to make it have an anti-reflection effect by optical interference, and it is mainly formed by laminating a SiO_2 film at upper layer and an ITO (InO added with Sn) film at lower layer. Because ITO is a conductive film, the anti-reflection film itself has an anti-static effect. Not only the anti-static effect, but also an electromagnetic shielding function is required for the surface treatment film of the Braun tube.

[0003] One of the wavelength selective absorption films is formed by adding a reddish violet group coloring material into a thin film, in order to absorb side bands of emission spectrum of green and red, and a Braun tube having a high contrast is provided (Toshiba Review, vol.45, No. 10, p831 (1990)).

SUMMARY OF THE INVENTION

[0004] The present invention relates to a display apparatus, particularly to a surface treating film of the display apparatus such as Braun tube, plasma display, and the like, for making the high definition display apparatus.

[0005] However, the prior art described above are insufficient for development of high definition Braun tube. Conventionally, a high definition Braun tube, whereon a surface treatment film having a low reflection, a low resistance, and a wavelength selective absorption effect, has not been developed, yet. For improving high contrast of the Braun tube, an anti-reflection characteristics is required, wherein the reflectance is controlled by laminating films having a wavelength selectivity by adding coloring material and different refractive indexes each other. It is well known that, when the coloring material is added, the refractive index is varied in the absorption wavelength region of the coloring material. When the anti-reflection is realized by optical interference effect, the optical interference effect is undesirably influenced, because the refractive index is varied by an abnormal dispersion of the refractive index of the coloring material. Therefore, the refractive index curve does not become flat, but generates waviness and an abnormal region to increase the refractive index and so on, and the performance as the anti-reflection film is deteriorated.

[0006] In consideration of variation in reflectance when the coloring material is added, when coloring materials of red, blue, and green are added, the refractive index is changed in respective of the absorption regions such as increasing once in accordance with decreasing the wavelength, and subsequently decreasing. Therefore, a relationship between the refractive indexes of the upper layer and that of the lower layer are inverted each other, and the control of the refractive indexes become difficult. When the coloring material is added to the laminated films, the refractive index curve is varied depending on whether the coloring material is added to the upper layer, or the lower layer. Accordingly, the reflectance can be decreased in a specified region by using change of refractive index of the coloring material, but in the region wherein the refractive index is inverted, the refractive index is increased because the refractive indexes of the films of the upper layer and the lower layer are inverted each other.

[0007] However, as a result, the refractive index of the film is decreased to smaller than the high refractive index of the original oxide film by adding the coloring material, because the refractive index of the oxide and the refractive index of the coloring material are averaged. Accordingly, as the reflectance curve, the value at the bottom is increased, because the difference of the refractive indexes of the upper and lower layers is decreased.

[0008] Furthermore, a low resistance film is necessary for the Braun tube, because functions of anti-static and electromagnetic shielding are required for the Braun tube. ITO is used most widely at present. However, if the coloring material is added, the resistance of the ITO is increased. The resistance tends to increase inversely to the requirement for low resistance, because the concentration of the coloring material tends to increase in order to enhance the wavelength selective absorption effect.

[0009] The object of the present invention is to provide a display apparatus formed a surface treatment film having a low reflection, low resistance, and wavelength selective absorption effect.

[0010] In order to achieve the above object, the present invention is characterized in that the display apparatus of the present invention is provided with a surface treatment film having a luminous transmittance equal to or less than 85 %, a luminous reflectance equal to or less than 2 %, and a flattened reflectance curve, of which absolute values of differential values are equal to or less than 2. Furthermore, the present invention is characterized in that the surface treatment film has selective absorption at approximately 450 nm, 570 nm, and 650 nm, and a sheet resistance equal to or

less than 10000 Ω/\square .

[0011] The high definition display apparatus having a wavelength selective absorption anti-reflective anti-static film of the present invention comprises a film laminated with at least three layers of protective film, conductive film, and absorption film on surface of the display plane, and the laminated film is composed of that the conductive film is arranged at a position closer to the surface of the display plane than the absorption film containing coloring material. The laminated film has a luminous transmittance equal to or less than 85 %, a luminous reflectance equal to or less than 2 %, a flattened reflectance curve, and a resistance equal to or less than 10000 Ω/\square . The conductive film is composed of at least one of metals selected from the group consisting of Ag, Pd, Pt, Cu, Cr, and Au. Furthermore, any one of ATO (SnO_2 added with antimony) and ITO, which are conductive oxide, can be used. The absorption film containing coloring material is composed of at least one of dyes and pigments selected from the group consisting of dyes and pigments having an absorption at 450 nm, dyes and pigments having an absorption at 570 nm, and dyes and pigments having an absorption at 650 nm.

[0012] The high definition display apparatus having a wavelength selective absorption anti-reflective anti-static film of the present invention comprises a film laminated with protective film, conductive film, and absorption film on surface of the display plane; the laminated film is composed so that a first layer from the surface of the display plane is the protective film made of mainly SiO_2 , a second layer is the conductive film composed of at least one of metals selected from the group consisting of Ag, Pd, Pt, Cu, and Cr, and a third film is the absorption film containing coloring material; and the laminated film has a luminous transmittance equal to or less than 85 %, a luminous reflectance equal to or less than 2 %, a flattened reflectance curve, and a resistance equal to or less than 10000 Ω/\square . Furthermore, the laminated film has an absorption equal to or less than 75 % at approximately 450 nm, an absorption equal to or less than 65 % at approximately 570 nm, and an absorption equal to or less than 75 % at approximately 650 nm; a luminous reflectance equal to or less than 1 %, a flattened reflectance curve, and a resistance equal to or less than 10000 Ω/\square .

[0013] In accordance with the present invention, a wavelength selective absorption anti-reflective anti-static film is utilized for display apparatus such as Braun tubes, plasma displays and so on.

[0014] The protective film is made of mainly SiO_2 , and aimed at maintaining the strength of laminated surface treatment film. The conductive film is made of metal or a conductive oxide for anti-static and electromagnetic shielding. Reflection is prevented by two layers of the protective film and the conductive film. The absorption film contains coloring material, and its function is to absorb wavelength selectively.

[0015] When coloring material is added, the refractive index of the film is varied depending on the absorption of wavelength by the coloring material. Therefore, if the reflection is prevented by an interference effect of light, the interference effect of light is influenced by variation of the refractive index. It is difficult to flatten the reflectance curve by decreasing the variation of the refractive index. In particular, if a large amount of the coloring material is added in order to increase the wavelength selective absorption effect, the variation of the refractive index in the absorption region is remarkable. The reflectance of the anti-reflection film is expressed as a luminous reflectance, which is an area of the curve obtained by multiplying the reflectance of the film in a visible light region of 380 nm-780 nm with the luminous sensitivities of the respective wavelengths. The luminous sensitivity is 1.0 at 555 nm. The luminous sensitivity is decreased as the wavelength takes distance from 555 nm, which is regarded as a standard, in both sides, and the luminous sensitivity becomes zero at 380 nm and 780 nm. Because the luminous reflectance is a product of the luminous sensitivity and the reflectance curve, the value at 555 nm is small, it becomes small only if the reflectance curve is flat, and not a U-shaped curve, but approximately a straight line. If change of the refractive index is increased by addition of coloring material, the reflectance curve does not become flat, and the luminous reflectance can not be decreased. In particular, when a red group coloring material is added, its absorption wavelength is in the range of 540-590 nm having a high luminous sensitivity, and influence of the change in the refractive index to the luminous reflectance is remarkable. As explained above, it is difficult to decrease the luminous reflectance by forming the wavelength selective absorption anti-reflection film by adding coloring material.

[0016] Therefore, in order to form an anti-reflection film having wavelength selective absorption characteristics by adding coloring material, the composition of the present invention is necessary. The anti-reflection characteristics can be obtained by utilizing interference effect of light generated by laminating films having different refractive indexes each other. As the number of laminated layers is increased, the intensity of light is decreased as the film comes close to bottom. Therefore, the reflectance curve can be flattened by arranging the film added with coloring material at a lower position in the layers as possible, because contribution of the film added with coloring material to the anti-reflection can be decreased. Furthermore, reflection of extraneous light can be increased by using a film having a high reflectance such as metallic film. Accordingly, if a metallic film is arranged at a position upper than the film added with coloring material, the intensity of extraneous light reached the film added with the coloring material is decreased. As the result, the contribution of the film to the anti-reflection effect can be decreased, and both the effects of wavelength selective absorption characteristics and the anti-reflection can be obtained with small number of laminated layers.

[0017] Here, the number of laminated layers means at least three laminated layers. In view of manufacturing, the number of laminated layers as small as possible is desirable. Manufacturing the wavelength selective absorption anti-

reflection film with a small number of laminated layers as possible can be achieved by using a film having an extremely large refractive index. The film added with coloring material generates a change in refractive index in the absorption wavelength region and decrease in the anti-reflection effect. However, when the film added with coloring material is arranged at a position lower than a high reflection layer, the intensity of reflected light at the boundary of the film added with coloring material is decreased remarkably, and the contribution to the interference of light can be decreased. Then, in accordance with the present invention, a metallic film such as Ag, Pd, Pt, Cr, Cu, and Au was used as the high reflection film. The metallic film has a small resistance, and operates as an electromagnetic shielding film. The reflectance is large, the intensity of extraneous light reached the film lower than the metallic film is small, and it is scarcely necessary to worry about light resistance of the coloring material for the wavelength selective absorption film. Generally, coloring material is decomposed by ultraviolet ray, and the light resistance is weak. Conventionally, pigment group coloring materials having a strong light resistance as a coloring material, but undesirable absorption characteristics, have been used as the coloring material. However, in accordance with the composition of the present invention, dye group coloring materials having a desirable absorption characteristics, but weak light resistance, can be used, and a high performance display apparatus having a preferable wavelength selective absorption characteristics can be manufactured.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018]

FIG. 1 is a partial cutaway side view of the Braun tube relating to the embodiment of the present invention;
 FIG. 2 is an observed results of reflectance and transmittance of the Braun tube relating to the embodiment of the present invention;
 FIG. 3 is a partial cutaway side view of the plasma display relating to the embodiment of the present invention;
 FIG. 4 is a schematic cross section indicating the composition of the surface treatment film relating to the embodiment of the present invention;
 FIG. 5 is a schematic cross section indicating the composition of the surface treatment film relating to the embodiment of the present invention;
 FIG. 6 is a schematic cross section indicating the composition of the surface treatment film relating to the comparative example of the present invention; and
 FIG. 7 is a schematic cross section indicating the composition of the surface treatment film relating to the comparative example of the present invention.

PREFERRED EMBODIMENTS OF THE PRESENT INVENTION

(Embodiment 1)

[0019] As an embodiment of the present invention, an example of manufacturing a Braun tube composing the display apparatus is explained, hereinafter.

[0020] FIG. 1 is a partially cutaway side view indicating a Braun tube 1 of the embodiment of the present invention.

FIG. 2 is a graph indicating an observed result relating to the relationship between each of a reflectance (indicated by the curve 13 in the figure) and a transmittance (indicated by the curve 14 in the figure) of the surface treatment film of the Braun tube with wavelength of light in the present embodiment. The high definition Braun tube 1 comprises a housing 2 made of glass, of which interior is evacuated. The housing 2 comprises a neck 3, a funnel portion 4 continued from the neck 3, and a face plate 5 sealed by frit glass. Outer peripheral side wall of the face plate 5 is wound with a metallic tension band 6 for anti-explosion. An electron gun 7 for discharging electron beam is arranged at the neck 3. A plurality of fluorescent members (generally fluorescent layers of three colors such as red, green, and blue applied in a dotted pattern or a stripe pattern), and a fluorescent screen 8, which is composed of black absorbing layers in a dotted pattern or a stripe pattern arranged between each of the fluorescent layers, are provided at inner surface of the face plate 5.

[0021] A CRT display apparatus (a cathode ray tube display apparatus) is composed by connecting the Braun tube 1 to display control circuits such as a horizontal and vertical deflection circuit, power source circuits, and the like. That is, in accordance with the cathode ray tube display apparatus, scanning by electrons, which are accelerated by the cathode voltage of the electron gun 7 of the cathode ray tube, is performed by flowing sawtooth current of horizontal cycles and sawtooth current of vertical cycles, respectively, to coils arranged in the vicinity of a path of the electron beam from each of horizontal and vertical deflection circuits, and image displaying is performed by forming a raster. The scanning lines by the accelerated electrons are projected to a luminescent screen 8 via shadow masks which are not indicated in the figure.

[0022] One of the feature of the present embodiment is that a wavelength selective absorption anti-reflective anti-static film 12 is provided at outer surface of the face plate 5 of the Braun tube 1.

[0023] A method for preparing the wavelength selective absorption anti-reflective anti-static film 12 is explained, hereinafter. A coating solution, which was prepared by adding a rhodamine group coloring material as a reddish violet group coloring material, Cu phthalocyanine as a blue group coloring material, and a yellow group coloring material to silica sol, was coated onto the surface of the Braun tube by a spin coating by 160 rpm, and dried at 60 °C for 5 minutes to form a SiO₂ film containing coloring material 9 on the face plate 5.

[0024] The composition of the solution is as follows:

SiO₂: 2 wt.%, sulforhodamine B: 0.05 wt.%, Cu phthalocyanine: 0.06 wt.%, ethanol: 20 wt. %, sodium fluorescein: 0.02 wt.%, water: 10 wt.%, and propanol: residual.

[0025] Then, a fine particle Ag-Pd dispersion liquid was applied by a spin coating method with 160 rpm, dried at 60 °C for 5 minutes, to laminate an Ag-Pd film 10 onto the SiO₂ film containing coloring material 9. Finally, silica sol was applied by a spin coating method with 160 rpm, dried at 60 °C for 5 minutes, to form a SiO₂ film 11.

[0026] Subsequently, the wavelength selective absorption anti-reflective anti-static film 12 was prepared on the face plate 5 by heating the laminated films to 160 °C with a velocity of 20 °C/min., heat-treating at 160 °C for 15 minutes, and cooling to room temperature with a velocity of 20 °C/min.

[0027] As the result, the surface resistance of the manufactured wavelength selective absorption anti-reflective anti-static film 12 was 350 Ω/□, and each of the transmittance and the reflectance was as indicated by respective of the curve 13 and the curve 14 in FIG. 2. A selective absorption film having transmittance of 75 % at 450 nm, 59 % at 570 nm, and 85 % at 650 nm, was obtained. Luminous transmittance of the film was approximately 85 %. A Braun tube having a reflectance of 5.8 % at maximum in the visible light region, 0.36 % at minimum with 555 nm, and a flat reflecting characteristics could be manufactured. The luminous reflectance of the film was 0.85 %. Absolute values of calculated differentials of the reflectance curve were equal to or less than 2. As explained above, the reflectance could be flattened, even if the wavelength selective absorption effect was added by adding coloring material.

[0028] Here, surface treatment films having various concentration of the coloring material in the film were prepared, and their contrast were calculated based on their RGB emission spectrum intensity and transmittance. It was revealed that the effect could be obtained if the luminous transmittance was in the range of 40-85 %. Then, it was decided that the luminous transmittance should be in the range of 40-85 %. However, if the luminous transmittance is in the range of 40-50 %, the brightness is decreased. Therefore, the range of 50-85 % is desirable.

[0029] Then, films having different transmittance each other were prepared by varying concentration of the coloring material to the absorption film, and their contrast were calculated by the same manner. It was revealed that the contrast was improved when each of the transmittance at 450 nm, 570 nm, and 650 nm was in the range of 85-40 %, 65-35 %, and 90-45 %, respectively. However, when the values at 450 nm and 650 nm were at least 75 %, and the value at 570 nm was at least 40 %, blackness of the film was diminished, and it became difficult to maintain color balance. The transmittance of the coloring material at each of 450 nm, 570 nm, and 650 nm is desirably in the range of 85-40 %, 65-35 %, and 90-45 %, respectively, but preferably in the range of 75-40 %, 65-40 %, and 75-45 % at 450 nm, 570 nm, and 650 nm, respectively.

[0030] The films having different thickness each other of the protective film, conductive film, and absorption film were prepared. It was revealed that, if the protective film, i.e. SiO₂ film, having a thickness of equal to or less than 150 nm, the conductive film having a thickness of equal to or less than 50 nm, and the absorption film having a thickness of equal to or less than 1200 nm were combined, the luminous reflectance became equal to or less than 1 %. However, the strength of the protective film is decreased when the film thickness is equal to or less than 40 nm, the resistance of the conductive film is increased when the film thickness is equal to or less than 20 nm, and decrease of the film strength and bleeding of the coloring material of the absorption film is generated, because the concentration of the coloring material is increased in order to obtain the designated transmittance when the film thickness is equal to or less than 300 nm. Accordingly, the protective film is desirably in the range of 150-40 nm, the conductive film is desirably in the range of 20-50 nm, and the absorption film is desirably in the range of 300-1200 nm.

[0031] An alloy of Ag-Pd was used for forming the conductive film. The conductive films having various ratio of Ag-Pd, respectively, were prepared. The surface resistance of the film was scarcely changed depending on the ratio of Ag-Pd, but difference in chemical resistance was generated each other depending on the ratio of Ag-Pd. It was revealed that, if the ratio of Ag-Pd was in the range of 6:4 - 9:1, the film was resistive against any of acids and bases such as HCl and NH₄OH. In some cases, an anti-chemical property of Braun tube surface becomes a problem depending on using environment or cleaning operation. Generally, the cleaning operation is performed using water and a neutral cleaner, and the using environment is in offices or the like. However, in some cases, acidic or alkaline cleaners are used in the cleaning operation, or the Braun tube is used in a laboratory where various chemicals are used. The surface treatment film of the present embodiment could be a film which was not restricted to any using environment, nor deteriorated by any cleaners.

[0032] The kind of the coloring material is not restricted to the above described materials, but any of dyes and pig-

ments, which have an absorption at the wavelength corresponding to any one of reddish violet, blue, and yellow, can be used. Similar results could be obtained by using any conductive film made of Ag, Pd, Cu, Pt, Cr, or Au, in addition to Ag-Pd.

[0033] Furthermore, the surface treatment film such as described above was applied to other display apparatus, for instance, a plasma display device.

[0034] The high definition plasma display manufactured in the present embodiment is composed of a structure indicated in FIG. 3. Electrodes for negative electrode 16 are formed on a back plane plate 15, and furthermore, display cells 20 composed of barriers 17, auxiliary cells 18, and priming spaces 19 are formed thereon. The display cells are coated with fluorescent materials 21, 22, 23 corresponding to respective of RGB. Electrodes for positive electrode 24 and auxiliary electrodes 25 are formed on an upper layer, and sealed with a front plane plate 26. The surface treatment film 27 was formed on the front plane plate 26. The composition of the surface treatment film was as same as that of the Braun tube indicated in FIG. 1.

[0035] The manufactured high definition plasma display was superior in selective absorption characteristics and reflection preventing characteristics, and improved in visibility.

[0036] As described above, it was revealed that the surface treatment film of the present embodiment could be applied to display apparatus other than Braun tube.

(Embodiment 2)

[0037] Next, a film, wherein an organic resin was added to the SiO_2 film containing coloring material at the lowest layer as indicated in FIG. 4, was manufactured. The method for manufacturing the film is explained hereinafter.

[0038] The SiO_2 film containing resin and coloring material 28 was formed on a face plate 5 by spin-coating a coating solution, prepared by adding acrylic resin and the coloring material into silica sol, onto surface of a Braun tube by 160 rpm, and drying at 60 °C for 5 minutes. Then, a Ag-Pd film 29 was laminated onto the SiO_2 film containing resin and coloring material 28 by applying a Ag-Pd fine particles dispersion solution onto the SiO_2 film, spin coating by 160 rpm, and drying at 60 °C for 5 minutes. Finally, a SiO_2 film 30 was formed on the Ag-Pd film 29 by spin coating a SiO_2 film onto the Ag-Pd film 29 by 160 rpm, and drying at 60 °C for 5 minutes.

[0039] The composition of the solution prepared by adding resin and coloring material was as follows:

SiO_2 : 2 wt.%, rhodamine B: 0.05 wt.%, ethanol: 20 wt.%, Cu phthalocyanine: 0.06 wt.%, water: 10 wt.%, sodium fluorescein: 0.02 wt.%, acrylic resin: 1 wt.%, and propanol: residual.

[0040] Then, a wavelength selective absorption anti-reflective anti-static film 31 was prepared on the face plate 5 by heating the laminated film to 160 °C with a velocity of 20 °C/min., heat-treating at 160 °C for 15 minutes, and cooling to room temperature with a velocity of 20 °C/min.

(Embodiment 3)

[0041] Next, a film, wherein ATO fine particles was added to the SiO_2 film containing coloring material at the lowest layer as indicated in FIG. 5, was manufactured. The method for manufacturing the film is explained hereinafter.

[0042] The SiO_2 film containing ATO and coloring material 32 was formed on a face plate 5 by spin-coating a coating solution, prepared by adding ATO fine particles and the coloring material into silica sol, onto surface of a Braun tube by 160 rpm, and drying at 60 °C for 5 minutes. Then, a Ag-Pd film 33 was laminated onto the SiO_2 film containing ATO and coloring material 32 by applying a Ag-Pd fine particles dispersion solution onto the SiO_2 film, performing spin coating by 160 rpm, and drying at 60 °C for 5 minutes. Finally, a SiO_2 film 34 was formed on the Ag-Pd film 33 by spin coating a SiO_2 film onto the Ag-Pd film 33 by 160 rpm, and drying at 60 °C for 5 minutes.

[0043] The composition of the solution prepared by adding resin and coloring material was as follows:

SiO_2 : 2 wt.%, rhodamine B: 0.05 wt.%, ethanol: 20 wt.%, Cu phthalocyanine: 0.06 wt.%, water: 10 wt.%, sodium fluorescein: 0.02 wt.%, ATO fine particles: 2 wt.%, and propanol: residual. The ATO used was a commercially available one, and ASR-4 made by Sumitomo Osaka Cement co. was used.

[0044] Then, a wavelength selective absorption anti-reflective anti-static film 35 was prepared on the face plate 5 by heating the laminated film to 160 °C with a velocity of 20 °C/min., heat-treating at 160 °C for 15 minutes, and cooling to room temperature with a velocity of 20 °C/min.

(Comparative example 1)

[0045] For comparison, a film, wherein a coloring material was added to the SiO₂ film at the uppermost layer as indicated in FIG. 6, was manufactured. The method for manufacturing the film is explained hereinafter.

[0046] The SiO₂ film 36 was formed on a face plate 5 by spin-coating a silica sol coating solution onto surface of a Braun tube by 160 rpm, and drying at 60 °C for 5 minutes. Then, a Ag-Pd film 37 was laminated onto the SiO₂ film 36 by applying a Ag-Pd fine particles dispersion solution onto the SiO₂ film, spin coating by 160 rpm, and drying at 60 °C for 5 minutes. Finally, a SiO₂ film 38 was formed on the Ag-Pd film 37 by spin coating a SiO₂ solution added with coloring material onto the Ag-Pd film 37 by 160 rpm, and drying at 60 °C for 5 minutes.

[0047] The composition of the SiO₂ solution added with coloring material was as follows:

SiO₂: 2 wt.%, rhodamine B: 0.05 wt.%, ethanol: 20 wt.%, Cu phthalocyanine: 0.06wt.%, water: 10 wt.%, sodium fluorescein: 0.02 wt.%, and propanol: residual.

[0048] Then, a wavelength selective absorption anti-reflective anti-static film 39 was prepared on the face plate 5 by heating the laminated film to 160 °C with a velocity of 20 °C/min., heat-treating at 160 °C for 15 minutes, and cooling to room temperature with a velocity of 20 °C/min.

(Comparative example 2)

[0049] Furthermore, for comparison, a film, wherein the coloring material was added into the Ag-Pd film as indicated in FIG. 7, was manufactured. The method for manufacturing the film is explained hereinafter.

[0050] A SiO₂ film 40 was formed on a face plate 5 by spin-coating a silica sol coating solution onto surface of a Braun tube by 160 rpm, and drying at 60 °C for 5 minutes. Then, a Ag-Pd film 41 was laminated onto the SiO₂ film 40 by applying a Ag-Pd fine particles dispersion solution added with the coloring material onto the SiO₂ film, spin coating by 160 rpm, and drying at 60 °C for 5 minutes. Finally, a SiO₂ film 42 was formed on the Ag-Pd film 41 added with coloring material by spin coating a SiO₂ film onto the Ag-Pd film added with coloring material 41 by 160 rpm, and drying at 60 °C for 5 minutes.

[0051] The composition of the solution prepared by adding resin and coloring material was as follows:

Ag-Pd fine particles : 1 wt.%, rhodamine B: 0.05 wt.%, ethanol: 20 wt.%, Cu phthalocyanine: 0.06 wt.%, water: 10 wt.%, sodium fluorescein: 0.02 wt.%, and propanol: residual.

[0052] Then, a wavelength selective absorption anti-reflective anti-static film 43 was prepared on the face plate 5 by heating the laminated film to 160 °C with a velocity of 20 °C/min., heat-treating at 160 °C for 15 minutes, and cooling to room temperature with a velocity of 20 °C/min.

[0053] Performance of the Braun tube surface treatment films prepared in the embodiments were evaluated. The performance evaluation was performed on transmittance, reflectance, surface resistance, strength, light resistance, and the amount of bleeding. Hereinafter, each of the performance evaluating methods is briefly explained.

[0054] The surface resistance was measured by a simplified surface ohm-meter (made by Nihon Yuka Co.) using a 4-pins probe or a 2-pins probe. The reflectance and the transmittance were measured by a spectrophotometer (U3500 made by Hitachi Ltd.) using an integrating sphere for eliminating an influence by random reflection. The film quality (surface roughness) was measured by a gross-meter (made by Horiba Seisakusyo Ltd.), and it had been confirmed that the film quality of any one of the films was at least gross value 98, and the influence of the random reflection was scarce. However, in some cases, the reflectance could be deemed as high performance owing to some influence of the random reflection. Therefore, the reflectance was measured exactly using the integrating sphere measuring system.

[0055] The film strength was measured by a eraser test. The film was rubbed with an eraser (5030 made by Lion Co.) with a load of 1 kg, and the strength was determined as the number of rubbing until the gross change of the film became at least 10 %.

[0056] The light resistance was determined by measuring a change in transmittance at 570 nm after irradiating the film with an ultraviolet ray (360 nm) of 4 mW/cm² for 300 hours.

[0057] The amount of bleeding was evaluated as a change in transmittance after forming the laminated layers taking the single layer of the film containing the coloring material as a standard. The transmittance at 570 nm after lamination becomes somewhat smaller than that of the single layer of the film containing the coloring material owing to the Ag-Pd film. Therefore, the measurement was performed on the single layer of the film containing the coloring material having the Ag-Pd film at its lower layer, and it was taken as the standard. The amount of bleeding ΔT was calculated by the following equation.

$$\Delta T = \frac{((\text{transmittance at 570 nm after lamination}) - (\text{transmittance at 570 nm of the single layer of the film containing the coloring material}))}{(\text{transmittance at 570 nm of the single layer of the film containing the coloring material})}$$

[0058] The results of performance evaluation of respective surface treatment film prepared as described above are indicated in Table 1.

Table 1

	Surface resistance (Ω/\square)	Transmittance (%)			
		450 nm	570 nm	650 nm	Luminous transmittance
Emb-1 ¹⁾	350	75	59	85	85
Emb-2	350	67	47	72	72
Emb-3	350	67	47	72	72
Com-1 ²⁾	4200	65	48	71	70
Com-2	8000000	82	78	89	86
	Reflectance (%)		Eraser test	Light resistance Δ	Amount of bleeding ΔT
	555 nm	luminous-reflectance			
Emb-1 ¹⁾	0.36	0.85	150	5	20
Emb-2	0.32	0.68	200	5	1
Emb-3	0.35	0.78	200	2	1
Com-1 ²⁾	2.3	3.8	50	50	0
Com-2	2.8	3.7	50	28	62

[0059] In the embodiments 1-3, the reflectance were less than 1 %, even if the transmittance were made small. Their differentials were less than 2, and flat reflectance curves were obtained. On the other hand, in the comparative examples 1-2, the transmittance were made small, but the reflectance were larger than 2 %, their differentials were larger than 3, and the reflectance curves were not flat. And, anti-reflection characteristics can not be obtained. In accordance with these results, it is revealed that the reflectance curve becomes flat by arranging the coloring material layer under the metallic film such as Ag-Pd film, and the anti-reflection characteristics can be made preferable. It is revealed from the results indicated in Table 1 that the light resistance can also be made preferable by arranging the coloring material layer under the metallic film. The metallic film has a high reflectance, and reflects incident light significantly at a boundary plane of the metallic film. Accordingly, transmittance of the incident light to the film at lower layer than the metallic film is decreased, and effects to the reflectance and deterioration of the coloring material by irradiation of ultraviolet ray can be suppressed. The light resistance is increased further if ATO fine particles are mixed into the coloring material layer, as indicated by the embodiment 3. Because, the ATO fine particles absorb ultraviolet ray, and the light resistance can be improved by not only ATO, but also any material, which is transparent and absorbs ultraviolet ray. For instance, ZnO, ITO, TiO₂, carbon, and the like are materials corresponding to the above material. Their effects could be confirmed by forming films with mixing actually these materials. However, as carbon is not transparent, its content must be suppressed as much as not to effect its transmittance.

[0060] In accordance with the embodiments 2 and 3, the film strength is increased more than that of the embodiment 1, and the amounts of bleeding are decreased. In a case when organic resin is added, the film becomes dense even in a dried condition, and the amount of bleeding is decreased. When treated at 160 °C, the adhesion force of the film is increased, because the resin is thermosetting resin, and as the result, strength of the film is increased. In accordance with the embodiment 1, the SiO₂ film and the Ag-Pd film are adhered each other, but metal and the SiO₂ film have not desirable wettability each other, and readily cause contact failure. On the other hand, in accordance with the embodiment 2, wherein an organic resin is added, generating the contact failure can be prevented, because a resin which is

used for adhesion of metal and glass is added. A resin such as acrylic resin, epoxy resin, phenolic resin, and the like could be used for the resin, and their advantages could be confirmed by preparing the film actually.

[0061] In accordance with the embodiment 2, wherein ATO was added, the bleeding was prevented by adsorbing the coloring material with fine particles of the oxide. Furthermore, the addition of fine particles is apt to be thought that the film strength is decreased, but actually, advantages as a filler are generated by optimizing the size and additive amount of the fine particles, and the film strength can be improved by relaxing internal stress of the film and preventing crack generation.

[0062] As explained above, the wavelength selective absorption characteristics can be added without lowering the reflection preventing characteristics by arranging the coloring material layer at a layer under the metallic film. And, it was revealed that the mechanical strength of the film could be improved by adding organic resin and fine particles to the coloring material layer. Furthermore, it was revealed that deterioration of the coloring material by ultraviolet ray could be prevented by arranging the coloring material at a layer under the metallic film, because the external light reached the coloring material after being weakened by the metallic film. Conventionally, if a material having no light resistance such as dyes was used with a high concentration, the material was deteriorated by irradiation of ultraviolet ray from fluorescent light. Therefore, it was difficult to use the dyes, and only one means was to use pigments. However, the pigments had an absorption peak broader than that of dyes, and the wavelength selective absorption characteristics was somewhat worse than that of the dyes. In accordance with the result of the present embodiment such that the light resistance could be improved, use of the dyes was made possible instead of the pigments which had been used widely, and it was found that the wavelength selective absorption characteristics could be improved. Therefore, it was revealed that Braun tubes having enhanced high contrast could be manufactured.

[0063] The above embodiments are explained with a film having a three layered structure, but the surface treatment film having a four-layered structure and more can be used within the scope of feature of the present invention. In the above case, another film can be arranged between the high reflectance layer and the absorption film. Some cases, another film can be arranged between the coloring material layer and the display plane.

[0064] As explained above, in accordance with a high definition display apparatus having an anti-static and anti-reflection film composed by laminating oxide or metallic thin films, at least three layers of oxide or metallic films having different reflectance each other are laminated on the surface of the display device, and the laminated film is composed so that an absorption film containing coloring material is arranged at a layer lower than the high reflectance film in view from the surface of the display device. Owing to the thin film of low resistance and high refractive index explained above, the surface treatment film having a wavelength selective absorption effect and an anti-static and an anti-reflection effect, and a luminous reflectance equal to or less than 2 % can be formed, and a high definition display apparatus having high contrast and safety, which can shield leak electromagnetic waves, can be provided.

[0065] In accordance with the present invention, a high definition display apparatus having high contrast and safety, which can shield leak electromagnetic waves, can be provided.

Claims

1. A display apparatus (1) comprising a film (12) on a display plane (5), wherein said film has:
 - a luminous transmittance (14) equal to or less than 85 %,
 - a luminous reflectance (13) equal to or less than 2 %, and
 - a flattened reflectance curve, of which absolute values of differential values are equal to or less than 2.
2. A display apparatus (1) as claimed in claim 1, wherein said film (12) has:
 - selective absorption at approximately 450 nm, 570 nm, and 650 nm, and
 - a resistance equal to or less than 10000 Ω/\square .
3. A display apparatus (1) comprising:
 - a laminated film (12) composed of at least three layers comprising a protective film (11), a conductive film (10), and an absorption film (9) at surface of a display plane (5), wherein
 - said laminated film (12) is constituted so that said absorption film (9) containing coloring matter is arranged at a position closer to said display plane (5) than said conductive film (10).
4. A display apparatus (1) as claimed in claim 3, wherein said laminated film (12) has:
 - a luminous transmittance (14) equal to or less than 85 %,

a luminous reflectance (13) equal to or less than 2 %,
 a flattened reflectance curve, of which absolute values of differential values are equal to or less than 2, and
 a resistance equal to or less than 10000 Ω/\square .

5 5. A display apparatus (1) as claimed in claim 3, wherein said conductive film (10) is composed of at least one of metals selected from the group consisting of Ag, Pd, Pt, Cu, Cr, and Au.

6. A display apparatus (1) as claimed in claim 3, wherein said coloring matter contained in said absorption film (9) is composed of at least one of dyes and pigments selected from the group consisting of dyes and pigments having
 10 an absorption at 450 nm, dyes and pigments having an absorption at 570 nm, and dyes and pigments having an absorption at 650 nm.

7. A display apparatus (1) comprising:

15 a laminated film (12) composed of at least three layers comprising a protective film (11), a conductive film (10), and an absorption film (9) at the surface of a display plane (5), wherein
 said laminated film (12) is constituted so that a first layer in the order from an outer surface of said laminated film is said protective layer (11) composed mainly of SiO_2 ; a second layer is said conductive layer (10) composed of at least one of metals selected from the group consisting of Ag, Pd, Pt, Cu, Cr, and Au, and a third layer
 20 layer is said absorption film (9) containing coloring matter.

8. A display apparatus (1) as claimed in claim 7, wherein said laminated film (12) has:
 25 a luminous transmittance (14) equal to or less than 85 %, a luminous reflectance (13) equal to or less than 2 %, and a resistance equal to or less than 1000 Ω/\square .

9. A display apparatus (1) as claimed in claim 7, wherein said laminated film (12) has:
 30 an absorption equal to or less than 75 % at approximately 450 nm;
 an absorption equal to or less than 65 % at approximately 570 nm,
 an absorption equal to or less than 75 % at approximately 650 nm,
 a luminous reflectance (13) equal to or less than 1 %, and
 a resistance equal to or less than 1000 Ω/\square .

35 10. A Braun tube (1) comprising:

40 a laminated film (12) composed of at least three layers (9, 10, 11) comprising a protective film (11), a conductive film (10), and an absorption film (9) at surface of a display plane (5), wherein said laminated film (12) is constituted so that said absorption film (9) containing coloring matter is arranged at a position closer to said display plane (5) than said conductive film (10).

11. A Braun tube (1) comprising a film on a display plane (5), wherein said film has:

45 a luminous transmittance (14) equal to or less than 85 %, a luminous reflectance (13) equal to or less than 2 %, and a flattened reflectance curve, of which absolute values of differential values are equal to or less than 2.

50 12. A display apparatus (1) as claimed in any one of claims from 1 to 9, wherein said display apparatus (1) is a plasma display.

FIG. 1

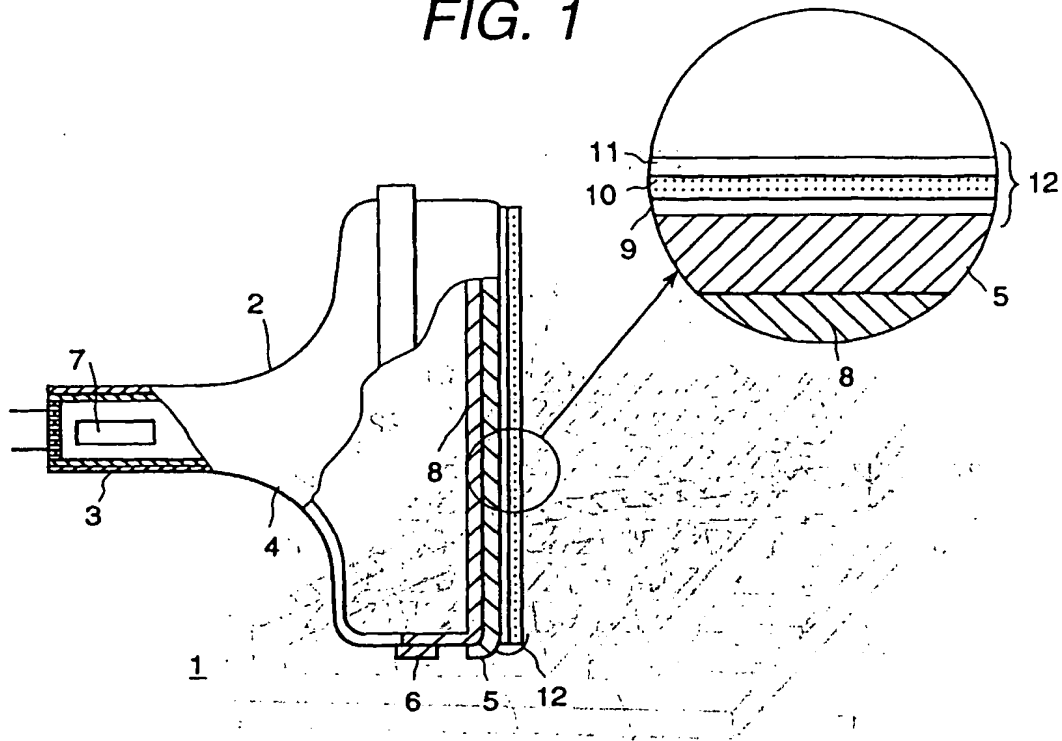


FIG. 2

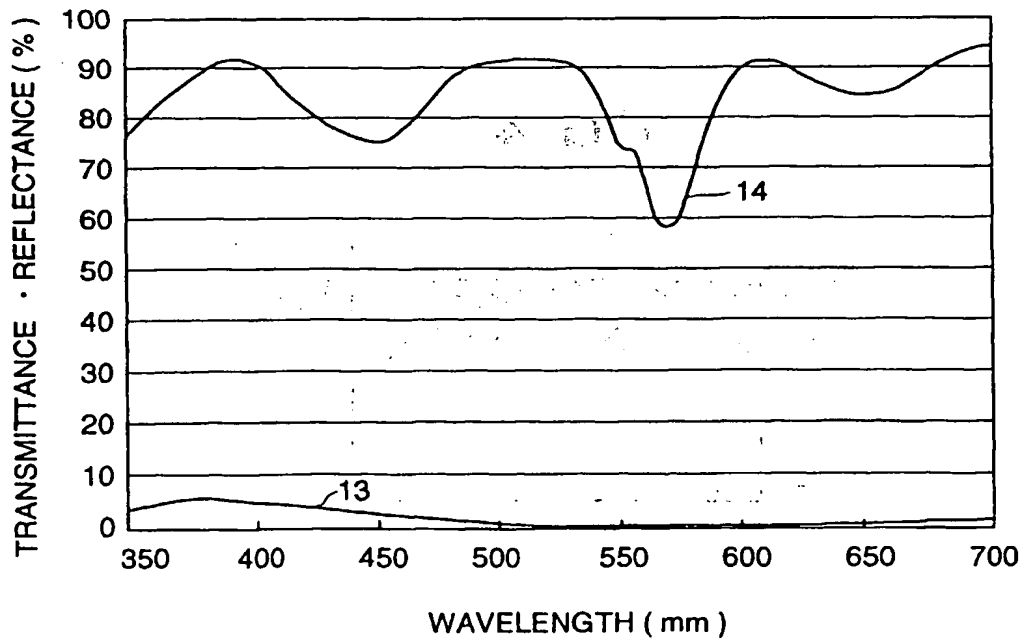


FIG. 3

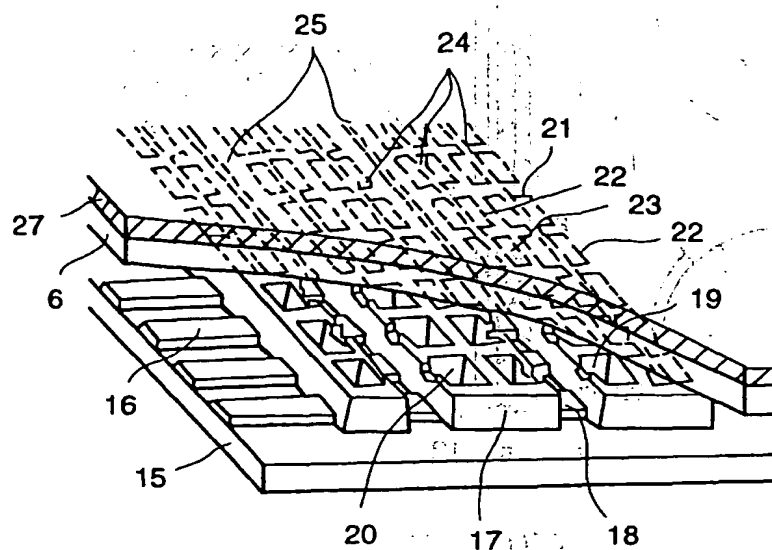


FIG. 4

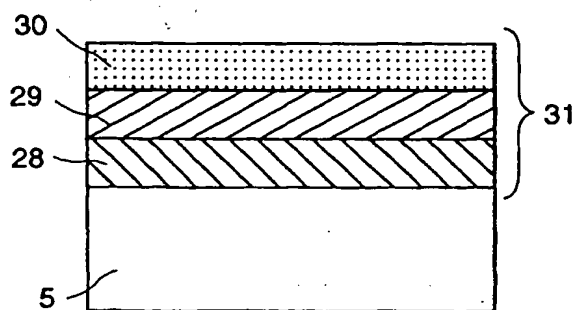


FIG. 5

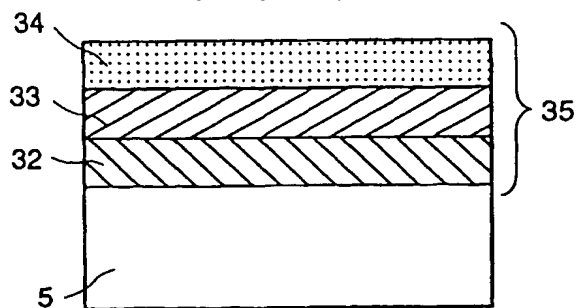


FIG. 6

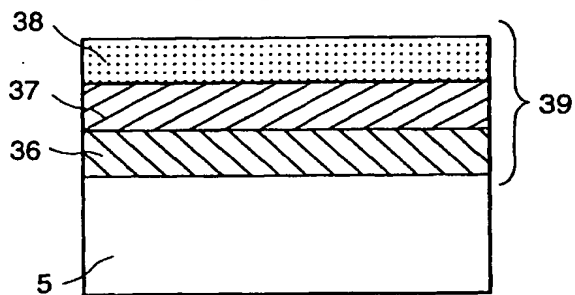
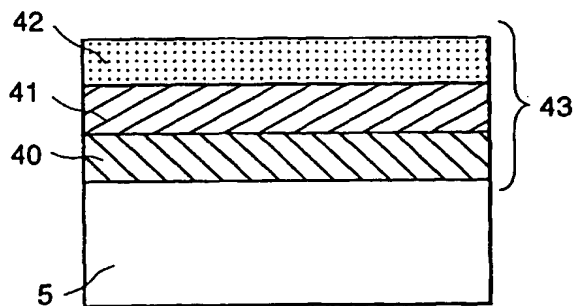


FIG. 7



THIS PAGE BLANK (USPTO)